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# Surface Spikes - A Perturbation of Growth Steps

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## ABSTRACT

During the growth of $NiBr_2$ crystals by sublimation, it has been observed that in addition to the mechanism of growth spirals a secondary mode of nucleation can occur. This is an accelerated growth which appears in the form of surface spikes on growth steps. The surface spikes may move as much as 50 times faster than the unperturbed growth steps. The mechanism of formation is believed to begin with the nucleation of a liquid droplet which wets the growth step and produces the accelerated growth from the liquid phase. The growth occurs at 500° C below the melting point of $NiBr_2$. It is believed that the nucleation of the liquid phase at these temperatures is impurity controlled.

# INTRODUCTION

During the growth of crystals by sublimation, it has been observed that in addition to the mechanism of growth spirals a secondary mode of nucleation can occur. This secondary nucleation occurs at localized positions along growth steps and produces a perturbation of the steps. At these locations the growth rate is more rapid than elsewhere along the growth steps resulting in the development of spikes in the surface of the crystal. Surface morphologies of this kind are referred to herein as surface spikes. This paper will present observations on the role of surface spikes in the growth of nickel bromide crystals by sublimation.

Surface spikes have been observed to occur as a result of supercooling: Kowarski[1] reported the formation of surface spikes during the growth of paratoluidine crystals from a saturated vapor on a substrate maintained at a few degrees (0-5 °C) below the melting point. He noted that highly mobile droplets would appear on the surface of a growing platelet, move about the surface until they came in contact with and wetted a growth step, and at these locations accelerated growth commenced in the form of a surface spike headed by the droplet. Lemmlein, et al,[2] extended these studies to supercooled systems of napthalene, diphenyl and diphenylamine. Their studies have shown a correlation between the velocity of growth of a surface spike and the radius of its attached droplet for a particular growth-step height. They also report surface spikes on SiC.

Surface spikes have been observed to occur as a result of polymerization in the vapor phase: Yoda[3] observed the appearance of droplets and the formation of surface spikes on molybdenum trioxide crystals at temperatures as low as three hundred degrees below the melting point (795 °C). The vapor phase of $MoO_3$ has been reported to consist principally of trimers,[4] $(MoO_3)_3$. Yoda suggests that the droplets on these crystals consist of "gas type" and "solid type" molecules, and that the gas type must undergo a transition to solid type before they can participate in crystal growth. The droplets serve as the place for this transition, and are stable at these low temperatures due to the lowering of their free energy which results from the mixing of two types of molecules.

Surface spikes have been observed to occur as a result of impurities; this paper will present observations on the formation of surface spikes on nickel bromide crystals and will present evidence suggesting that the mechanism of formation is impurity controlled.

The vapor-liquid-solid (VLS) mechanism of Wagner and Ellis[5] is closely allied to the mechanism of surface-spike formation reported herein. In fact, the only significant differences appear to be: (1) the mode of nucleating the liquid phase, (2) the characteristics of the surface where "wetting" by the droplet has occurred, and (3) the morphology of the resultant growth (three dimensional in the VLS case, two dimensional in the case of surface spikes). In all of the examples cited above the presence of three phases are required to produce the surface-spike morphology.

# PREPARATION OF CRYSTALS

Crystals of nickel bromide (dendrites and platelets) have been grown by sublimation in the presence of an inert carrier gas (He or A).[6] Commercial NiBr$_2$[7] and material synthesized in this laboratory from nickel (99. 9%) and bromine (99. 5%) have been used. Sublimation temperatures usually ranged from 625 to 700 °C and the crystals grew on the inside surface of a silica tube that was placed in a region of the tube furnace where the temperature during no-growth conditions had been found to extend from 480 to 575 °C. Optical studies were made with an ordinary metallurgical microscope at magnifications of ca. X75 and X150 using reflected light and having the crystals mounted on a two-circle goniometer. The crystals were removed from the growth chamber and examined in the ambient atmosphere. No special mounting was required for electron microscopy. For electron-microprobe analyses, the specimens were fastened with a drop of silver paint to aluminum disks that had been coated with graphite. They were subsequently coated with a thin layer of carbon in an evaporator.

## MORPHOLOGY

Figure 1A shows a typical platelet with growth spirals and surface spikes on the spirals. The dark lines represent surface structure on the near side of the platelet while the low-contrast lines represent structure on the far side of the platelet. Typically the platelets are thin and transparent and both surfaces lie within the depth of focus of the microscope objective. The large droplets seen in this figure are principally water that has been adsorbed from the ambient atmosphere. The central region of this figure, where no dark-line structure is visible (representing the near side), is assumed to be a smooth plane within the resolution of the optical microscope. A thickness contour of the platelet, in this region, can be obtained from a monochromatic light interferogram. Figure 1B shows the same area under monochromatic illumination. Regions of constant contrast are interpreted as regions of constant thickness and, hence, it is deduced that the surface spikes are protrusions from growth steps maintaining the outermost terrace of the originating growth step as their bounding surface. Figure 2 is an oblique drawing of a surface spike.

Figure 3A shows the tip of a dendrite, on which a growth spiral has developed, with surface spikes and droplets. Figure 3B is an enlargement of the central region of the same spiral. Nickel bromide has the $CdCl_2$ structure with the bromine ions forming close-packed planes which are the growth-habit planes of the dendrites and platelets. The axis normal to these planes has three-fold symmetry and this symmetry is seen in the orientation of the surface spikes in Fig. 3. The low contrast structure seen in Fig. 1 and Fig. 3 reveals that the growth directions of the surface spikes on opposite sides of these platelets are rotated 60°. Such rotation does not always occur. Occasionally surface spikes are seen on trigonally symmetric polygonal spirals. Figure 4 is an example of this kind of morphology. When this occurs the surface spikes grow in directions perpendicular to the sides of the polygonal growth pyramid. Surface spikes that develop on growth pyramids (spiral or polygonal) are usually oriented according to the point-group summetry of the axis perpendicular to the habit plane.

As seen in Fig. 2, the sides of surface spikes are usually straight with no variation in width of the surface spike where it crosses a growth step. At the base of a surface spike, where it joins with a growth step, several structures are possible. If the surface spike is oriented perpendicularly to the growth step the geometry at the base
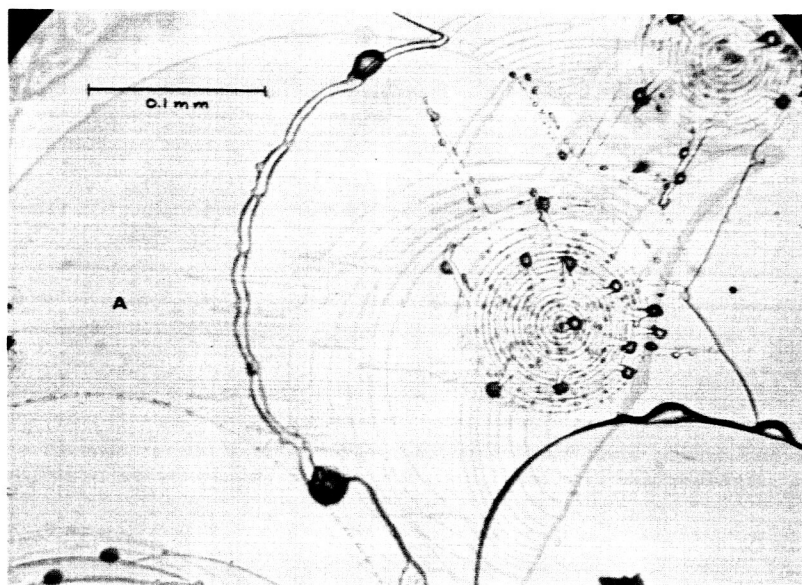
Figure 1A.  Bright-field photomicrograph of NiBr$_2$ platelet.  A surface
spike originating at the base of a growth spiral on the far
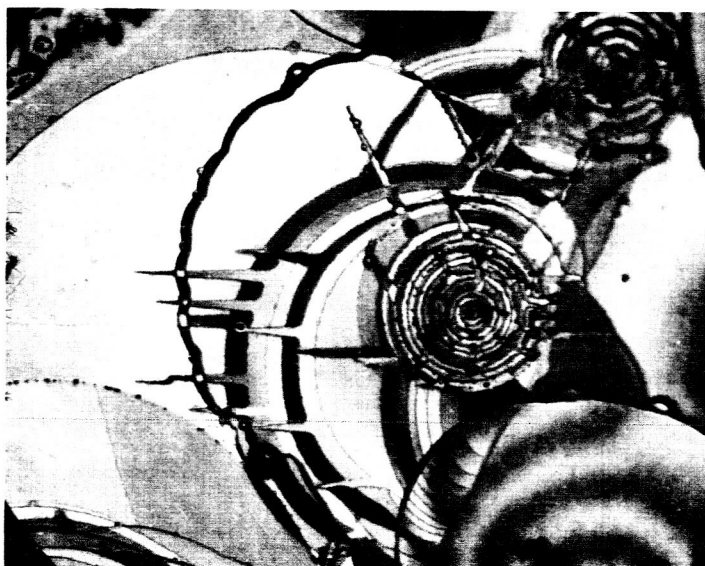side of the platelet is labeled A.



Figure 1B.  Monochromatic interferogram of the region shown in
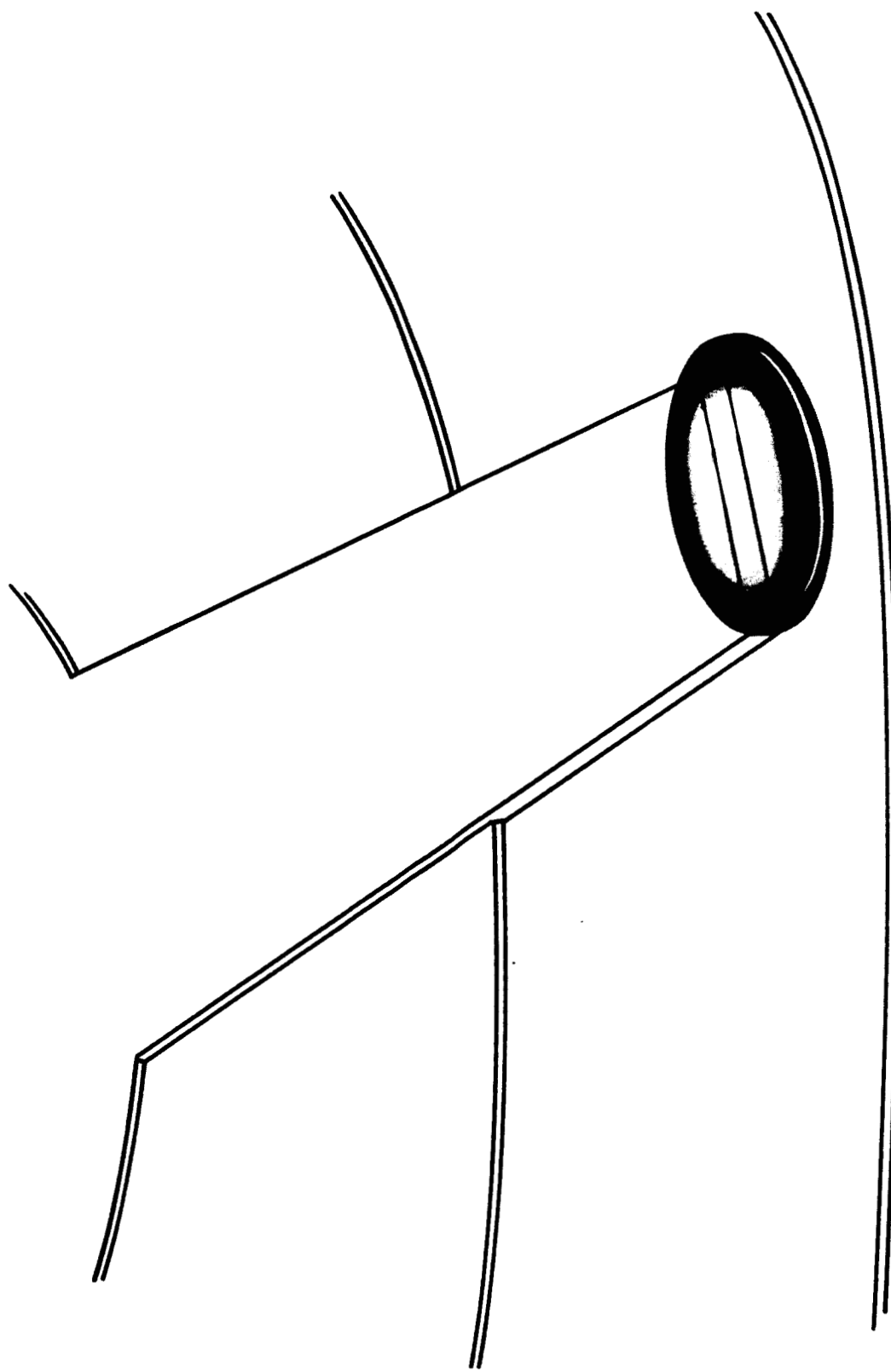Figure 1A made at 546 m$\mu$.

Figure 2.   Oblique drawing of a surface spike, with a liquid droplet attached, growing on a growth spiral.
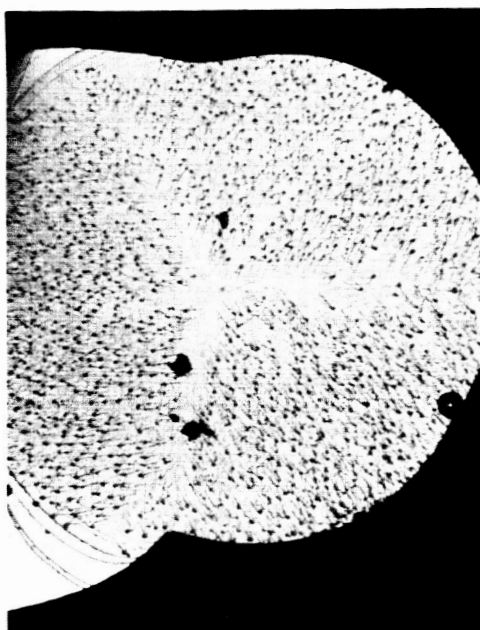
Figure 3A.   Photomicrograph of the tip of a NiBr$_2$ dendrite showing trigonally symmetric fields of surface spikes on a growth spiral
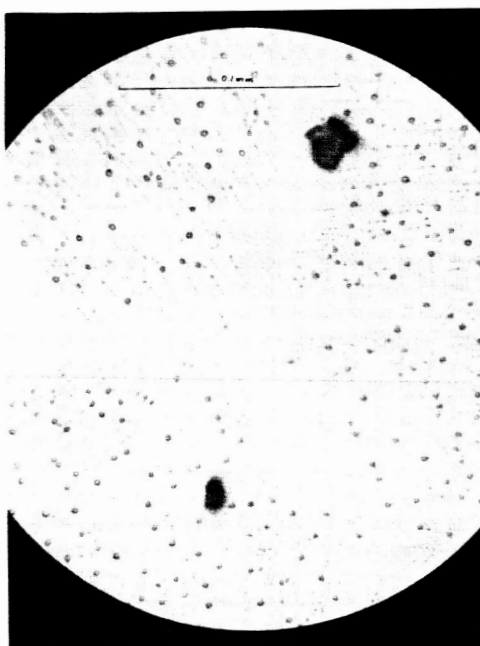


Figure 3B.   Enlargement of the central region of Figure 3A.   Low contrast outlines of surface spikes on the far side of the crystal can be seen.
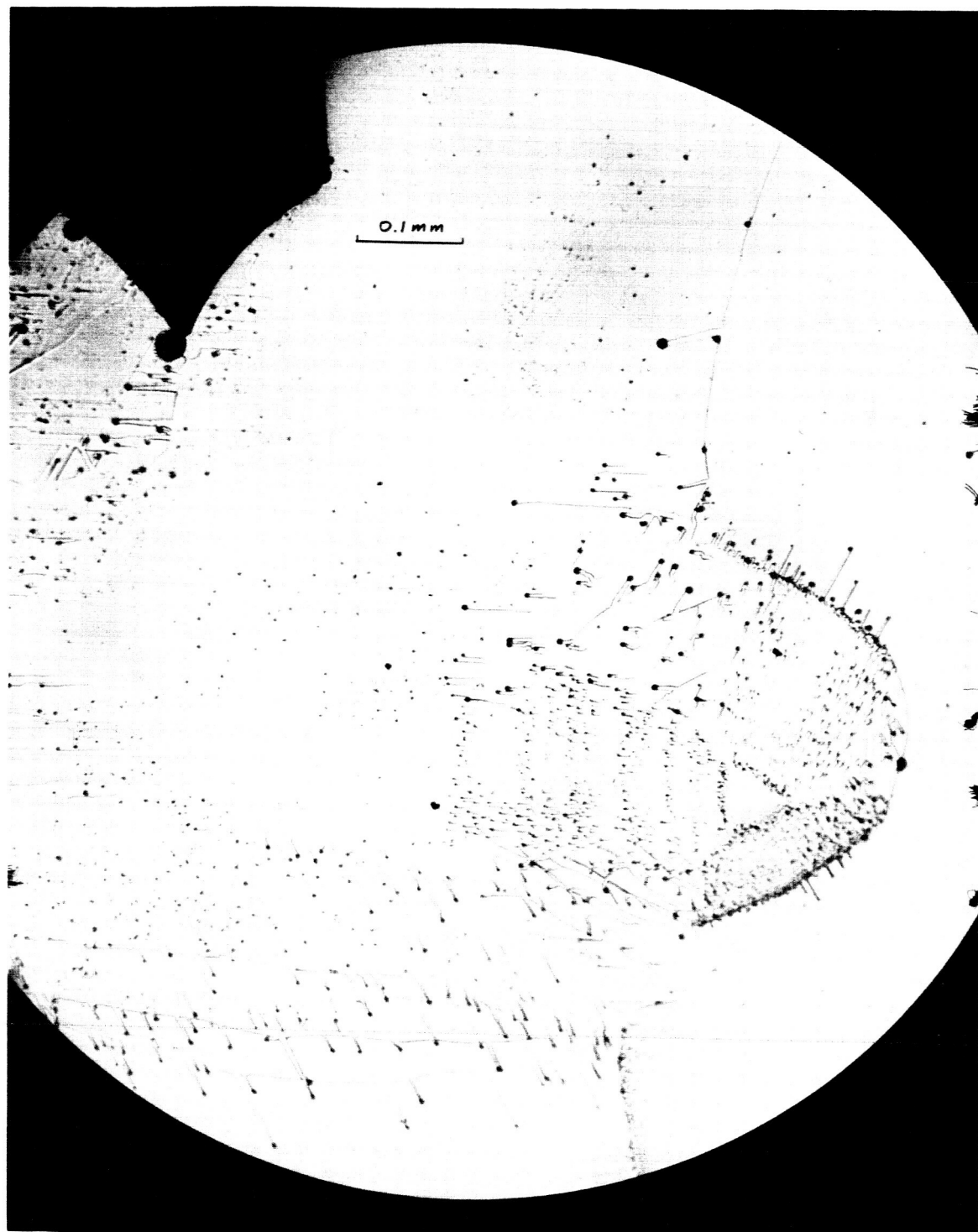
Figure 4.    Surface spikes on a trigonally symmetric growth pyramid on a $NiBr_2$ platelet.  This specimen was carbon coated for electron-microprobe analysis.

consists of the intersection of the straight-edged spike with the natural shape of the growth step or the growth step is joined to the surface spike by several short straight segments. These segments have the appearance of crystallographically oriented facets. If the surface spike is oriented obliquely to the growth step the base on the acute-angle side develops a more advanced front of growth than that on the opposite side. The surface spikes that develop on a particular growth pyramid have approximately the same length with the exception of those that grow from the base of the pyramid (or those that cross the basal step). The latter are typically much longer than the former; note the example labeled A in Fig. 1A.

The height of a surface spike begins as the step height of the originating growth step and increases by integral amounts with each crossing of a growth step (see Fig. 2). The step heights of these pyramids vary from values so small that the steps cannot be seen with an optical microscope, and the optical interference pattern of the pyramid can barely be detected as a few broad diffuse concentric circles of color, and range to values so large that the steps are easily seen with a low power microscope.[8] Typical of the values for the growth steps studied most frequently in this work would be of the order of a few hundred molecular layers in magnitude.[7]

Surface spikes do not always develop on growth pyramids but may even occur more frequently at random growth steps on dendrites and platelets. When the surface spikes are not associated with a growth pyramid their morphology is ill-defined. The direction of growth may be random with frequent unrelated changes or it may vary from one crystallographic orientation to another. Figure 5 is an example of such growth on dendrites. Usually the velocity of growth of the surface spike is appreciably higher when it originates from the base of a growth pyramid or from a random growth step. Occasionally the width of the surface spike will fluctuate periodically as shown in Fig. 6. When this occurs there is usually evidence that two surface spikes have followed the same path.

It is believed that a liquid-phase is an essential part of the development of a surface spike and that each surface spike has a droplet attached at its tip. However, it is not easy to observe the unadulterated droplet. The larger droplets seen in the accompanying figures are principally water. $NiBr_2$ is hygroscopic and it is apparent that the tips of the surface spikes exhibit the greatest hygroscopic activity.

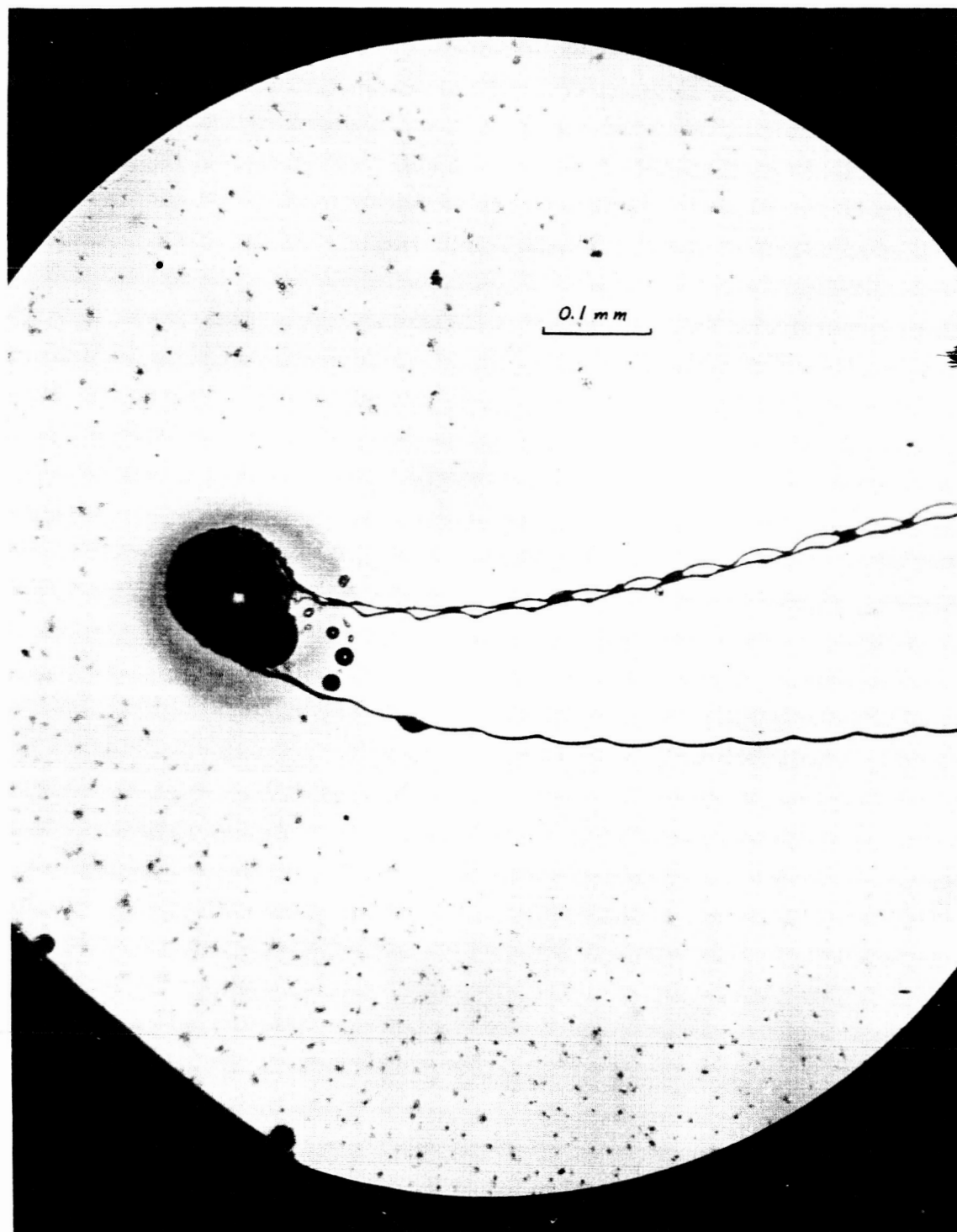Figure 5.    Surface spikes with random directions of growth on NiBr$_2$ dendrites.

Figure 6.    Surface spike, on a NiBr₂ platelet, with a fluctuating width.    This specimen has been carbon coated for electron-microprobe analysis.

Areas believed to be related to droplets have been observed with an electron microscope.[9] By comparing photomicrographs with electron micrographs an estimated diameter of ca. 1 micron has been made for the droplets. This is the reason for suggesting such a large droplet in Fig. 2.

# CRYSTAL GROWTH

The rate of formation of the solid phase within a surface spike can be represented by two velocities; $V_s$, the longitudinal velocity and, $V_w$, the transverse velocity of the surface spike. The transverse velocity leads to the tapered shape of the surface spike and the ratio of the velocities, $V_w/V_s$ can be obtained from the tangent of the half-angle defined by the sides of the surface spike. When the growth step at the base of the surface spike is curved, suggesting no anisotropy in the velocity of the unperturbed step, it is assumed that the transverse velocity of the surface spike is equal to $V_0$ the velocity of the unperturbed step. This situation leads to upper limits on the velocities which can only be obtained when other growth steps are sufficiently far removed so that competition for material within a given diffusion zone does not occur. Where conditions are appropriate, for considering these characteristic velocities to be the same among several surface spikes, their dimensions provide a comparative measure of their relative ages. Among surface spikes growing in a group on the same growth pyramid, their basal widths are usually uniform suggesting that they were all nucleated at approximately the same time, see Figs. 1 and 3. Their lengths show some variation which are probably the result of differences in individual droplets. Furthermore, it is clear, especially in Fig. 3, that the surface-spike growth has occurred only during the latter stages of platelet growth. A surface spike, of comparable length to the others on the same pyramid, has formed on the fourth step from the top on the near side of the crystal, and on the first step on the far side.

A rather striking feature about surface spikes growing on the same growth pyramid is that those at the base of the pyramid are usually longer than those growing elsewhere on the same pyramid. This may suggest that the longer surface spikes are the more characteristic of this mode of growth while the shorter ones were prevented from attaining equivalent lengths due to their crossing of growth steps and consequential increases in thickness. An examination of the dynamics of surface spike growth will demonstrate the relationship between the various velocities. Consider the growth of a surface spike on a growth pyramid whose steps have a uniform spacing, S. Let $V_{s1}$ be the velocity with which the surface spike crosses the first terrace between the zeroth and first steps in an interval of time $\Delta t_1$. Then $V_{s2}$, $V_{s3}$, ... $V_{sn}$ and $\Delta t_2$, $\Delta t_3$, ... $\Delta t_n$, will represent the corresponding velocities and time intervals for succeeding terraces. Let $V_{w0}$ be the transverse velocity of the base of the surface spike along the zeroth step. Then $V_{w1}$, $V_{w2}$, ... $V_{wn}$ will represent the corresponding velocities of the intersections of the surface

spike with succeeding steps (see Fig. 7). Let w be the width of the blunt end of the surface spike and assume it to remain constant. The velocity of the unperturbed region of the growth steps is taken as $V_0$ and is assumed to be the same for each step on the same growth pyramid. The y-coordinate axis is oriented along the center line of the surface spike, with its origin at the starting point of the surface spike and $X_n$ represents the X-coordinate of the intersection of the side of the surface spike with the $n^{th}$ step. Then

$$X = \frac{w}{2} + V_{w0}t$$

$$X_1 = \frac{w}{2} + V_{w1}(t - \Delta t_1); \qquad \Delta t_1 = \frac{S}{V_{s1} - V_0}$$

$$X_2 = \frac{w}{2} + V_{w2}(t - \Delta t_1 - \Delta t_2); \quad \Delta t_2 = \frac{S}{V_{s2} - V_0}$$

$$X_n = \frac{w}{2} + V_{wn}(t - \sum_{i=1}^{n} \Delta t_i); \quad \Delta t_n = \frac{S}{V_{sn} - V_0}$$

The difference in the intercepts of two successive steps, divided by the terrace width is the tangent of the half-angle, $\alpha$, of the tapered surface spike in that region.

$$\frac{X_{n-1} - X_n}{S} \equiv \tan \alpha_n = \frac{V_{w,n-1}}{V_{s,n} - V_0} \tag{1}$$

The accompanying photomicrographs show surface spikes having a constant taper suggesting that $\alpha_n$ is independent of n. This is readily obtained from eq. (1) by letting $V_{sn} = V_s$ and $V_{w,n-1} = V_w$.

$$\text{Then} \quad \tan \alpha_n = \frac{1}{\frac{V_s}{V_0} - 1} \tag{2}$$

However, the observation that surface spikes at the base of a growth pyramid are longer than those elsewhere on the same pyramid does not derive from eq. (2). We need to obtain $\alpha_n$ independent of n while $V_{sn}$ is a function of n. Intuitive arguments for the functional dependence have not produced the desired result. If we assume that with each step crossed
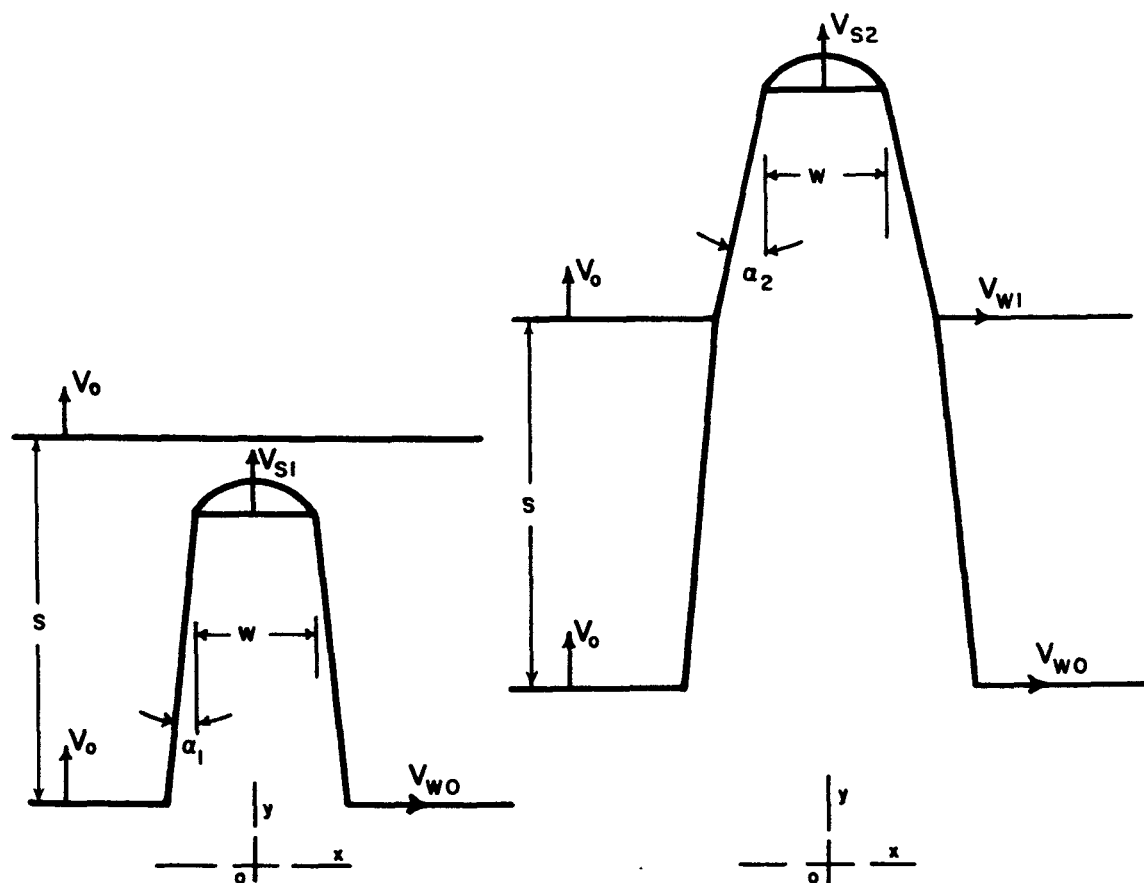
Figure 7.    Two stages in the growth of a surface spike on two neigh-
boring growth steps moving with constant spacing. The
left-handed drawing represents a stage of growth after
nucleation of the surface spike growth and before it has
reached the next step of the spiral. On the right-hand the
surface spike has crossed the first step.

the longitudinal and transverse velocities for the new terrace and step are decreased from their former values in proportion to the increase in the cross-sectional areas at the end and sides of a surface spike, we may express the appropriate velocities as $V_{sn} = \frac{1}{n} V_{s1}$ and $V_{w,n-1} = \frac{1}{n} V_{w0}$. And, letting $V_{w0} = V_0$, we find

$$\tan \alpha_n = \frac{1}{\frac{V_{s1}}{V_0} - n} \tag{3}$$

If we maintain the same dependence for $V_{sn}$ but assume that the increase in lateral-face area of the surface spike has no effect on the transverse velocity, $V_{wn}$, then we may take $V_{wn} = V_{w0}$. This situation could obtain if the kink density in the lateral faces is sufficiently small so that concentrations of the sources (the vapor and the adsorbed molecules) are not altered by the growth process. Thus we find (again letting $V_{w0} = V_0$ )

$$\tan \alpha_n = \frac{n}{\frac{V_s}{V_0} - n} \tag{4}$$

The desired property for $\alpha_n$ (independent of n) could be obtained by letting $V_0$ become a function of n, but only at the expense of maintaining uniformity of terrace widths - a consequence that is inconsistent with the observations. The assumption that $V_{sn}$ should decrease inversely as the surface spike increases in thickness is in agreement with the observations of Lemmlein, et al,[2] for surface spikes of varying thickness but not growing on growth pyramids. The assumptions leading to eq. (2) are in disagreement with this same observation. Further studies are in progress to resolve these questions.

The interaction of surface spikes, ahead of a growth step, can be an important phase of the accelerated growth. In the case of $NiBr_2$ three directions are available for the development surface spikes and all three occur when a growth step passes through the appropriate orientation. On the other hand, all three directions may develop in a field of surface spikes which initially have only one growth direction, Fig. 8, is an expample. This can occur when successive steps are sufficiently far removed so that very long surface spikes develop in

Figure 8.    Dark-field photomicrograph of interacting surface spikes on a NiBr$_2$ platelet.   The magnification is the same as that of Figure 6.   The longer individual surface spikes have tapers giving $V_S/V_W \sim 30\text{-}60$.

the first orientation. Then secondary nucleation on the sides of these produces the other two orientations. All of the surface spikes in this field have the same thickness and are growing on the same terrace. As the interactions among various orientations proceeds, enclosed areas are developed between interacting surface spikes which are gradually reduced until they vanish. The rate of closure should be determined by $V_w$ and not by $V_{S1}$. The surface spikes in Fig. 8 have tapers of $2°$ to $4°$ leading to $V_s/V_w \sim 30$ to $60$.

Surface spikes offer a mechanism for the development of hopper-type morphology as discussed by Dekeyser and Amelinckx.[10] Instead of representing the super-saturation along the growth step as a continuous function of position, as did Dekeyser and Amelinckx, one need only use a delta-function to localize the driving force represented by the droplet. A hopper-type morphology will develop if the surface spike periodically changes direction and retraces its same path. Such periodic change has been observed by Yoda,[3] but the surface spike did not retrace the same path and instead proceeded to fill in the region bounded by its first circuit. However, the hollow nickel whiskers reported by Gold[11] have both of these characteristics. A tapered surface spike and droplet are clearly visible in Fig. 1 of his paper. Hopper growth has been looked for on $NiBr_2$ crystals but has not been found.

# MECHANISM OF GROWTH

Since the formation of surface spikes on $NiBr_2$ crystals occurs at ca. 500°C below the melting point of $NiBr_2$, supercooling effects are ruled out as a mechanism for droplet formation.

The possibility of polymerization within the vapor phase of $NiBr_2$, as a mechanism for droplet formation according to the model of Yoda,[3] has also been ruled out. Schoonmaker, et al,[12] performed mass spectrographic analyses of $NiBr_2$ and $NiCl_2$ by Knudsen effusion techniques, in the temperature range between 440 and 700°C, and report no dimeric species of either molecule. If higher polymers were present then ion currents for low polymer fragments should have been observed. Samples of $NiBr_2$, from this work, were sent to a mass spectrographic laboratory to be analyzed, by Knudsen effusion techniques, for the presence of trimers in the vapor phase. The results were negative.

In the presentation of the experimental investigation of $NiBr_2$ the presence of a droplet phase has been incorporated as an integral part of the accelerated growth. However, it should be pointed out that such droplets have not been observed in situ at the growth temperatures (such studies have not been made). Occasionally it is difficult to determine whether a droplet exists at the tip of a surface spike. In view of these observations the possibility of accelerated growth without the aid of a droplet has been considered. It is necessary, for such a process, that in a localized region of a growth step that the rate of increase of the solid phase be markedly greater than elsewhere along the growth step. It has been suggested that this could happen during the growth of $NiBr_2$ if the vapor phase contained an excess of $Br_2$ and if the tri-valent state of Ni occurred at localized sites along a growth step. Then three atoms of Br could be incorporated into the solid phase for each Ni atom, instead of the usual two. There is evidence that $NiBr_2$ dissociates in the high temperature zone of the growth chamber which would provide excess $Br_2$ in the growth zone. Although this model produces an increase in molecular volume of each nickel-bromine molecule it is not clear that the kink density and the surface diffusion kinetics available to the tri-valent molecule will lead to the observed magnitude of accelerated growth ($V_s/V_w \sim 50$). On the other hand, there are two reasons to reject this model: only the divalent states of the nickel halides are stable at room temperature and higher valency states would seem to be more compatible with lower rather than higher temperatures. Secondly, the conditions for $NiBr_2$ dissociation are present throughout the growth

process at the growth temperature yet there is evidence that surface spikes are nucleated only after a period of initial growth by other mechanisms. This model has also been rejected in favor of an impurity effect.

It is proposed that the phenomenon of accelerated growth, as discussed herein with specific references to $NiBr_2$, can be explained adequately on the basis of an impurity model. The essential details of the model are as follows: the initial stages of growth may be considered as involving two phases (vapor and solid) and may be treated according to the Burton, Cabrera and Frank[13] theory for growth steps. The vapor phase is assumed to possess an impurity constituent which has a lower solubility in the solid phase. As growth of the solid phase progresses the impurity constituent is rejected by the solid phase, in amounts governed by the solubility, and tend to collect on the surface. The surface acts as a sink for the impurity and the surface concentration of the impurity increases in time. Eventually the adsorbed impurity constituent reaches a sufficient concentration in the surface two-dimensional gas of the growth species that localized nucleation of the liquid phase of the growth species occurs.[14] It is, therefore, necessary that the impurity species have the property of adequately lowering the free energy of the growth species to produce the appropriate melting point. Both temperature and concentration can affect the nucleation and a phase diagram of the two component system may be necessary to interpret their variations. Once the droplet is formed it may or may not be mobile on the crystal surface; if mobile it can move to a growth step and attach to the growth step, and if it is not mobile the growth step can overtake it. Once the droplet has wetted a localized region of the growth step accelerated growth can proceed at the liquid-solid interface.

The time-element of this model (i.e., the period required to accumulate a sufficient concentration of adsorbed impurities to nucleate a liquid droplet) is suggested by the observation that young surface spikes are observed on old growth pyramids. The liquid phase is introduced to provide a mechanism for more rapid phase transformation than occurs through the kinetics of surface diffusion of a two-dimensional gas and its exchange with kink sites. At least an order of magnitude increase over the unperturbed velocity of a growth step is needed. (Sometimes the surface spike velocity, $V_s$, is so high that very long surface spikes are found whose taper cannot be measured with any accuracy.) The impurity constituent is needed to provide a two component system having a sufficiently low solidus.

Impurity studies have been made of surface spikes on $NiBr_2$ crystals (grown from commercial material) by means of electron-microprobe analysis.[15] Regions of the droplet, the surface spike, and the surrounding terrace were compared. The characteristic X-ray intensities for Ni and Br remained constant as the electron beam moved from the terrace to the surface spike, but both decreased when the beam passed over the droplet. Four impurities were identified in the droplet region that were not found elsewhere: Cu, Co, Mn, and Fe.

# CONCLUSION

Accelerated growth via surface spikes is characterized by two growth rate phenomena occurring ahead of the unperturbed growth step. The projection of a surface spike from a step or a growth pyramid with its apparent discontinuities in growth rate, and the interaction of surface spikes ahead of a growth step. The history of the surface spike relative to other surface morphology can be inferred from a comparison of its position on growth pyramids, and by comparing the width of its base to the width of the adjoining terrace of the growth pyramid. The localization of the perturbation and the associated increase in velocity can be accounted for by postulating the existence of a liquid droplet attached to the growth step and having the growing species as one of its constituents. It is proposed that a droplet of the liquid phase is nucleated as a mixture of the growing species with one or more impurities which have accumulated at the surface of the crystal.

# ACKNOWLEDGMENTS

# FOOTNOTES

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14. The mechanism for the increase of surface concentration of impurities, the subsequent nucleation of a liquid phase, and impurity analyses will be discussed in a second paper on surface spikes.

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